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Characterisation of hot material erupted from Mahanadi riverbank using EDXRF and XRD techniques

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Abstract : A detailed mineralogical study was carried out on iron-rich hot material oozed out from Mahanadi riverbank, Cuttack in Orissa. Both qualitative and quantitative estimation of the multi-elements of this complex material was carried out by Energy Dispersive X-ray Fluorescence (EDXRF) technique. Among the analysed elements, iron is found to be in highest concentration *i.e.* 18.8%, whereas K, Ca, Ti and Mn are present as minor constituent, and V, Cr, Co, Cu, Zn, Se, Rb, Sr and Pb are present in trace quantities. Different crystallographic phases like maghemite (γ-Fe_2O_3), hematite (Fe_2O_3), chromite ($FeCr_2O_4$), cuprospinel ($CuFe_2O_4$), cuprite (Cu_2O), zhanghengite (CuZn), ramsdellite (MnO_2), mullite ($Al_6Si_4O_3$), anatase (TiO_2), marokite ($CaMn_2O_4$), zincochromite ($ZnCr_2O_4$) and baddelete (ZrO_2) have been observed prominently. Some low intense lines of potassium chlorite ($KClO_2$) and karelianite (V_2O_3) are also identified by the X-ray powder diffraction (XRD) technique.

Keywords : Hot material, EDXRF, XRD

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The chemical composition of lava erupted from a volcano, gives valuable information on the nature of melted rock source, the process of melting and the processes that modified the composition of the original magma [1]. Again, geological and petrological study of hot materials like lava may reveal the character and history of the resulted events. The most common elements found in magmatic ore found in the volcano sites are iron, chromium, nickel, platinum, iridium, palladium, osmium, ruthenium and rhodium. Platinum is a valuable metal among the observed trace elements. Again, complexes like chrome ($FeCr_2O_4$), a spinel is a very important industrial material found in magmatic deposition. Iron rich [2-6] hot materials are mainly available in form of magmatic sulphides [2, 5] or oxides.

Eruption of hot material occurred for the first time in Orissa on 12th November 2002 from Mahanadi riverbank [7], Cuttack in India that attracted the attention of many academicians and scientists. In order to unfold some information regarding the above hot materials, an attempt has been made to characterise these hot materials using two well known X-ray techniques like energy dispersive X-ray fluorescence (EDXRF) and X-ray diffraction (XRD). The present note is based on the results obtained from EDXRF and XRD to get information on elements from the igneous rock as well as its complex form. EDXRF technique is simple, non-destructive, simultaneous and multielemental in nature and it can be used for the present purpose quite relevantly. Again, X-ray diffraction technique is frequently used for petrographic characterisation like Fourier Transform Infrared Spectrometry, Scanning Electron Microscopy *etc.*

EDXRF technique is most widely used to assess the elemental composition of a sample. The technique is multi-elemental and non-destructive in nature and therefore relatively fast as

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compared to the other analytical technique. A significant number of elements present in a variety of samples: solids, powders and even liquids, can be detected and quantified by this technique. An advantage of EDXRF technique is that it allows analyzing solid samples with little or no sample preparations. In EDXRF technique, heating of the samples does not occur and temperature seldom exceeds 50^{0}C and generally much lower. Hence, heat sensitive and volatile elements can be better studied by this technique with respected to other conventional quantitative methods.

The hot material was sun-dried before thoroughly crushing into fine powder. With 500 mg of the fine powdered sample, a binder such as pure cellulose was added in 1:1 ratio. Then they were thoroughly mixed and homogenized and pressed into pellets of 1-inch diameter in a KBr press. Pellets were also prepared from the Certified Reference Materials (CRM) such as for irradiation in the EDXRF-system as standards to check the validity of this method.

Again, sample was taken from central part of the bulk hot material and ground into fine powder about 500-mesh size. Then this powdered hot material was uniformly packed in an aluminium cavity of 20 × 15 × 2 mm^3 groove by the help of a glass slide to make a flat sample for X-ray powder diffraction study.

Energy dispersive X-ray fluorescence analysis was performed using MoK X-rays generated from a secondary molybdenum target of an EDXRF system. The EDXRF system incorporates a low power aircooled X-ray tube (50-watt) as an excitation source with tri-axial geometry [8]. The X-ray tube was operated at 25 kV and 0.6 mA. The X-rays from the tube were exposed on a molybdenum secondary exciter and the characteristic K-X-rays of molybdenum (17.8 keV, the weighted average energy of the MoK$_\alpha$ and K$_\beta$ lines) were used to excite the characteristic X-rays of elements present in all the samples. The fluorescent X-rays were collected using a Si (Li) detector having a thin Be window (8-micron thickness) and processed by a high-resolution amplifier. The spectra were recorded by using a PC-based multi-channel analyzer [9]. The photo-peak areas in each spectrum were evaluated using the computer program AXIL [10] supplied by International Atomic Energy Agency (IAEA). The intensities of the characteristic X-rays of elements in the sample are proportional to the original elemental concentrations in the sample, which were evaluated by least squares fitting method using the AXIL program.

Moreover, high-resolution X-ray diffraction data were collected by using a Philips analytical X-ray instrument, X'Pert-MPD, available at National Institute of Technology (NIT), Rourkela employing Bragg–Brentano parafocusing optics. Data have been collected in $\theta - 2\theta$ scanning mode with a scanning rate of 2^0/min. Incident line focus CuK$_\alpha$ - radiation from a high power ceramic tube operated at 40kV and 30mA were initially collimated through Soller slit (0.04 rad), fixed divergence slit (2^0) and mask (10 mm) before irradiating the sample. The diffracted beam from the sample was well-collimated by passing it through a programmable anti- scattering slit (2^0), programmable receiving slit (0.3 mm) and Soller slit (0.04 rad) before getting it reflected by the curved graphite crystal (002) monochromator of radius 225-mm. A Xe-gas filled proportional counter was mounted on the arm of the goniometer circle of radius 200-mm to collect diffracted X-ray signal.

The EDXRF spectrum of the hot material is presented in Figure 1 and the concentrations of observed elements are provided in Table 1. It can be inferred from Table-1 data that the hot material contains elements like K, Ca, Ti and Mn with lower percentage. Fe amount is very high *i.e.* 18.8%, which is the major constituent in the hot material. V, Cr, Co, Cu, Zn, Se, Rb, Sr and Pb were found to be the trace elements in the hot material

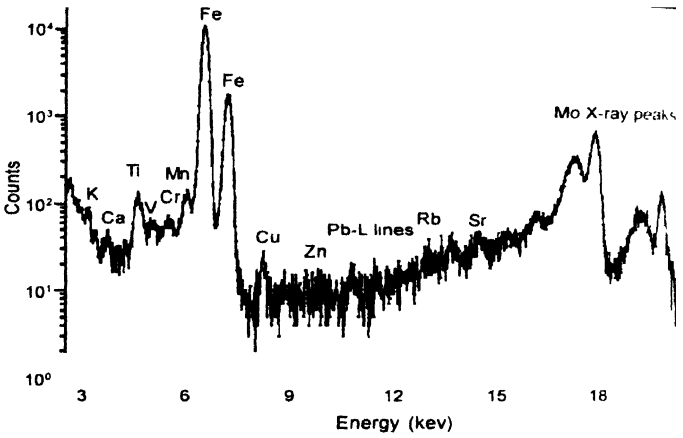

Figure 1. EDXRF spectrum of hot material

Table 1. Concentration (mass basis) of various elements in the hot mate (in *ppm unless otherwise specified)

Elements	Concentration
K	0.49 %
Ca	0.30 %
Ti	0.75 %
V	503.4
Cr	383.8
Mn	0.13 %
Fe	18.80 %
Co	101.1
Cu	127.2
Zn	25.5
Se	5.7
Rb	18.3
Sr	17.2
Pb	5 3

*ppm: parts per million

From the powder diffraction study (Figure 2), different crystallographic phases of the material were identified using

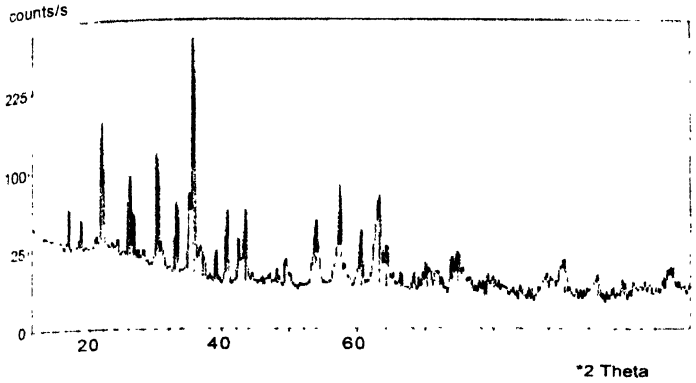

Figure 2. Spectrum of a fine powdered X-ray diffraction sample

PCPDFWIN, V1.3 (JCPDS 1997). It is bit difficult to identify all the crystallographic phases in the material because of its complexity. Peak search was carried out using Philips X'Pert Graphics software. Full widths at half maximum (FWHM) of the diffraction peaks were estimated using "Profit" for profile fitting, supplied by Philips Analytical X-ray, Netherlands. Crystallographic parameters like glancing angle, d-spacing of the planes, relative intensity, Miller indices and FWHM of identified phases are listed in the same table. Crystallite dimension (D_{hkl}) of identified phases are calculated using corrected Scherrer formula [11,12] as

$$D_{hkl} = \frac{K\lambda}{(B-b)\cos\theta},$$

where B is the line width, b is the instrumental broadening, K is the shape factor (=0.9), θ is the Bragg angle and λ is the wavelength of CuKα1 (1.54056 Å).

Table 2. Crystallographic phase identified from X-ray powder diffraction

Sl. No	Phase	2 θ degree	d-value (Å)	$h\,k\,l$	Relative Intensity (%)	FWHM	Crystallite dimension (D_{hkl}) (Å)
1	γ-Fe_2O_3	18 3967	4.81870	111	6 79	0.155	519
	(Maghemite)	30.3041	2 94696	220	32 56	0 220	374
		35 6952	2 51326	311	100 00	0 292	286
		43 3633	2 08494	400	14 33	0 266	321
		53 8625	1 70069	422	11 60	0 496	180
		57.3649	1 60490	511	22 86	0 450	201
2	Fe_2O_3	26 1285	3 40766	211	22 05	0 150	544
	(Hematite)	33 1419	2 70082	104	15 22	0 284	292
		49 3245	1 84601	024	3.66	0 406	215
		90 4204	1 08537	226	3 93	0 253	446
3	$FeCr_2O_4$	37.0607	2.42373	222	2 36	0.155	541
	(Chromite)	73.8633	1 28196	533	4 25	0 306	325
4	$ZnCr_2O_4$	74.6238	1 27077	533	5 25	0 295	339
	(Zincochromite)	90 4204	1 08537	731	3 93	0 253	446
5	Cu_2O	42.4203	2.12908	200	7 12	0.221	386
	(Cuprite)						
6	CuZn	63 0365	1 47346	200	19 31	0 447	209
	(Zhanghengite)	95 3334	1 04199	220	1 99	—	—
7	MnO_2	21 7788	4.07741	101	46 39	0 307	264
	(Ramsdellite)	35.0500	2.55803	301	17.68	0 292	285
8	$Al_6Si_4O_3$	16 3410	5 41996	110	12 26	0 142	565
	(Mullite)	25.8500	3.44374	210	15.20	0.150	544
9	TiO_2	48.1483	1 88832	200	1 48	0.092	946
	(Anatase)						
10	$CaMn_2O_4$	39.1007	2 30183	031	4.24	0.200	422
	(Marokite)	40 6710	2 21653	222	13.78	0.248	342
		60.4272	1 53069	012	9.48	0 252	365
		64.1686	1.45017	360	6.14	0 380	246
11	ZrO_2	26.6338	3.34414	-	9.99	0 124	658
	(Baddelete)						

From X-ray powder diffraction study of above hot material, nearly fourteen different crystallographic phases are identified using PCPDFWIN, V1.3. Out of fourteen phases, eleven important phases with the crystallite dimension are shown in Table 2. Among, these phases, iron is in the form of oxides like maghemite (γ -Fe_2O_3)(JCPDS 39-1346), hematite (Fe_2O_3) (JCPDS 24-0072), chromite ($FeCr_2O_4$)(JCPDS 34-0140), and cuprospinel ($CuFe_2O_4$)(JCPDS 25-0283) [13]. Maghemite (311) is found as the most intense (100%) peak in the diffractogram. Crystallite dimension of maghemite and hematite are varying from 201-519 Å and 215-544 Å, respectively. Diffraction peaks of cuprospinel ($CuFe_2O_4$) of (511) and (440) planes are found to superimpose with γ -Fe_2O_3 (511) and CuZn (200) planes, respectively. Chromium phases like chromite ($FeCr_2O_4$)(JCPDS 34-0140) and zincochromite ($ZnCr_2O_4$)(JCPDS 22-1107) are also found out from the above analysis. A number of different phases like cuprite (Cu_2O)(JCPDS 01-1142), zhanghengite (CuZn)(JCPDF 02-1231), ramsdellite (MnO_2)(JCPDS 39-0375), mullite (Al_6Si_4 O3)(JCPDS 15-0776), anatase (TiO_2)(JCPDS 02-0387), marokite ($CaMn_2O_4$)(JCPDS 16-0709) and baddelete (ZrO_2)(JCPDS 02-0464) are also observed prominently. Some low intense potassium chlorite ($KClO_2$)(JCPDF 02-1320) and karelianite (V_2O_3)(JCPDS 34-0187) phases are also observed in the diffraction pattern. From the above estimation of crystallite dimensions, we observed TiO_2 has largest crystallite dimension of 946 Å as compared to others. The density of the hot material was found to be 3.0134 gm/cm^3 as determined using specific gravity bottle.

Generally, earth's inner core materials are solid mixtures of iron and nickel with a higher density as compared to outer core materials. From the above study, iron was found to be the major constituent in the hot material. It was found that the studied hot material contains various minor/trace elements like K, Ca, Ti, V, Cr, Mn, Co, Cu, Zn, Se, Rb, Sr and Pb. The complex forms of iron exist in the form of γ -Fe_2O_3, Fe_2O_3, $FeCr_2O_4$, $CuFe_2O_4$ and some other complex forms of the specimen like Cu_2O, CuZn, MnO_2, Al_6Si_4 O_3, TiO_2, $CaMn_2O_4$, $ZnCr_2O_4$ and ZrO_2 have be observed prominently. Some low intense lines of $KClO_2$ a V_2O_3 are also identified by X-ray powder diffraction techniq Non-observance of Ni or its phase confirms us that the h materials are basically erupted from outer core region of t earth. The result was also ascertained by density measureme

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